DOI: https://doi.org/10.26896/1028-6861-2023-89-10-19-24

NOVEL STATIONARY PHASES BASED ON EPOXIDIZED POLYSTYRENE-DIVINYLBENZENE FOR THREE MODES OF LIQUID CHROMATOGRAPHY

© **Anastasiia V. Gorbovskaia, Ilsina I. Talipova, Arsenii A. Timichev, Anna S. Uzhel*, Oleg A. Shpigun**

Lomonosov Moscow State University, Department of Chemistry, 1 bld. 3, Leninskie gory, Moscow, 119991, Russia; *e-mail: anna_uzhel@mail.ru

Received August 10, 2023. Revised August 10, 2023. Accepted August 24, 2023.

Mixed-mode stationary phases based on epoxidized copolymer of styrene and divinylbenzene have been obtained by amination with methylamine, further alkylation with 1,4-butanediol diglycidyl ether and opening the terminal oxirane rings with dimethylethanolamine. To evaluate the effect of the number of anchor amino and diol groups on the degree of hydrophilization of resins, the quantity of reagents was varied. Polymerization of glycidol in the functional layer at an increased pH of the reaction medium was carried out for additional shielding of the substrate. It was found that increasing the number of anchor amino groups is promising for increasing hydrophilicity in suppressed ion chromatography and hydrophilic interaction liquid chromatography modes, while polymerization of glycidol increases the degree of substrate shielding. The applicability of the most hydrophilic adsorbent in three HPLC modes was demonstrated. Novel mixed-mode stationary phase allows the separation of six nucleosides and nitrogenous bases by hydrophilic interaction liquid chromatography, 7 alkylbenzenes by reversed phase liquid chromatography, and 20 organic and inorganic anions by suppressed ion chromatography.

Keywords: mixed-mode stationary phases; poly(styrene-divinylbenzene); suppressed ion chromatography; hydrophilic interaction liquid chromatography; reversed phase high performance liquid chromatography.

Introduction

The creation of mixed-mode stationary phases is an intensively developing direction in the field of high performance liquid chromatography (HPLC) [1 – 7]. Various functional groups of such phases ensure the retention of analytes via a combination of two or three mechanisms, which allows their use in different chromatography modes, such as ion-exchange, reversed phase (RP), and hydrophilic interaction liquid chromatography (HILIC). Most often mixed-mode resins are based on silica that is stable in a limited pH range; as a result, such adsorbents can't be used in highly sensitive suppressed ion chromatography (IC) mode [8, 9]. The transition from silica to a poly(styrene-divinylbenzene) (PS-DVB) with a high degree of cross-linking that is stable over the entire pH range and is suitable for working with 100% organic solvents can solve this problem. PS-DVB is widely used for synthesis of anion and cation exchangers for suppressed IC, and some of these phases were successfully used in other HPLC modes. Due to the presence of hydrophobic substrate they were applied in RP HPLC [10 – 13], while the attachment of hydrophilic ion-exchange layers made it possible to use them in HILIC mode [10 – 12, 14 – 16].

Fixing the hydrophilic anion-exchange layer on the PS-DVB surface requires preliminary substrate modification for the introduction of anchor groups. In classic approaches to chemical modification of polymer substrates, such as chloromethylation or Friedel – Crafts acylation, anchor groups are formed not only on the substrate surface, but also inside the particle in a hydrophobic environment [8, 17]. As a result, simple functional layers attached to these substrates can't provide proper shielding degree, which leads to low peak symmetry and efficiency of hydrophobic and weakly hydrated anions. Besides, such phases lack of separation ability and provide the separation of almost only standard inorganic anions [8, 18]. For improving the characteristics of chemically modified anion exchangers, multi-stage synthesis and grafting complex functional layers is necessary. However, in HILIC mode even resins with complex grafted layers exhibit abnormally high retention of hydrophobic analytes, namely p-toluenesulfonate and phenylalanine [12, 15].

On the other hand, modification of residual double bonds that are predominantly located on the surface of polymer particles [19, 20] leads to obtaining hydrophilic resins [21 – 24]. Using

m-chloroperbenzoic acid for the double bonds oxidation to epoxide groups is preferable due to reagent availability, short duration and high yield of the reaction [14, 25, 26]. Polymerization of glycidol in the functional layer can be applied for additional shielding of the substrate [27]. Additional hydrophilization of the substrate surface can be achieved by the hydrolysis of remaining after modification epoxy groups [23, 28]. This approach provided significant reduction of nonionic interactions in IC mode and allowed one to decrease the retention of hydrophobic analytes and to increase the retention of hydrophilic ones in HILIC mode. However, grafting bulk polyamine on the substrate surface resulted in low efficiency of the phases due to slow mass transfer. Presumably, the attachment of simpler and thinner layer to epoxidized PS-DVB can help to obtain mixed-mode resins with increased efficiency and separation ability.

Thus, the aim of the work was to create mixed-mode stationary phases via covalent attachment of hydrophilic branched layers on the surface of epoxidized PS-DVB. Polymerization of glycidol in the structure of the resin was applied for additional substrate shielding.

Experimental

Instrumentation. "Memmert" Thermostate (Memmert GmbH & Co. KG, Schwabach, Germany), "Laboport" vacuum pump (KNF Neuberger, Tranton, New Jersey, USA), "Sapphire 6580" ultrasonic bath (Sapphire, Moscow, Russia), "Eurostar" mechanical stirrer (IKA-Werke, Staufen, Germany) were used for the syntheses.

A Dionex ICS 2100 Ion Chromatography system equipped with an isocratic pump and a conductivity detector with a suppressor was used for IC with potassium hydroxide as an eluent. A Dionex UltiMate 3000 Liquid Chromatography system equipped with a gradient pump, an autosampler, and a diode array detector and a Vanquish Flex liquid chromatograph equipped with a gradient pump, an autosampler, a column thermostat, with fluorescence and diode array detectors were used with mixture of water, acetate, or formate and acetonitrile as an eluent. Absorbance of Tanaka test's analytes, nucleosides, nitrogenous bases and alkylbenzenes was measured at 254 nm. Data acquisition and processing were controlled by Chromeleon 7.0 and 7.3 (Dionex part of Thermo Scientific) software. Injection volume for all model mixtures was 20 µl. The columns were tested at 30°C. The 100 × 4.0 mm i.d. stainless steel columns were used as housing for the studied stationary phases and slurry packed at 400 bar using a K-1900 pump (Knauer, Berlin, Germany) in accordance with ref. [15].

Reagents. All chemicals had reagent and analytical-reagent grade and were purchased from Sigma-Aldrich (Russia) and TCI Chemicals (Japan). PS-DVB microspherical particles (cross-linking degree 50%, particle size 5.5 ± 0.5 µm, average pore diameter 4 nm, average pore volume 0.6 cm^2/g, surface area 660 m^2/g) were identical to those used in ref. [5, 12, 14 – 16, 25].

Synthesis of the stationary phases. Epoxidized PS-DVB was obtained according to ref. [25] and was used for creation of all obtained resins. For synthesis of resin EB-DMEA x5 amination with methylamine, hydrolysis of residual epoxy groups and further alkylation with 1,4-butanediol diglycidyl ether was conducted in the same conditions as in ref. [25]; final amination with dimethylethanolamine was carried out for 1 h at 60°C. The amount of amine corresponded to the amount of 1,4-butanediol diglycidyl ether. Resin EB-DMEA x1 was synthesized with decreased in 5 times reagents amount at all steps starting from epoxidized PS-DVB. Resins EB-DMEA x1 Gl and EB-DMEA x5 Gl were obtained via glycidol treatment of EB-DMEA phases. Polymerization of glycidol was conducted according to work [25]. The scheme of PS-DVB modification is shown in Fig. 1.

Results and discussion

In this work two ways of epoxy groups' modification were applied to create stationary phases on the base of hydrophilized PS-DVB. The first one was the amination of these groups with methylamine to obtain anchor amino groups for subsequent attachment of the functional layer (Fig. 1, way 1). For additional increasing the shielding degree and hydrophilicity of the PS-DVB surface, the remaining epoxy groups were hydrolysed forming diol groups (Fig. 1, way 2). It's known that glycidol polymerization can be used for additional substrate shielding [14, 15, 25, 27]. In this study glycidol can polymerize both in the functional layer and on the surface of the substrate with diol groups. Thus, it was interesting to evaluate the influence of anchor amino and diol groups' amount on the hydrophilization degree of the resulting adsorbents. For that purpose phase EB-DMEA x1 with branched functional layer and its analogue EB-DMEA x5 with increased reagents amount were synthesized. Obviously, resin EB-DMEA x1 contained higher number of diol groups. After treatment of both phases with glycidol resins EB-DMEA x1 Gl and EB-DMEA x5 Gl were obtained.

Predictably, an increase in the reagents amount led to the growth of ion-exchange capacity for both types of phases EB-DMEA and EB-DMEA Gl (Table 1). However, this growth was not proportional to the reagents amount increase, which can be explained by the smaller number of available ep-

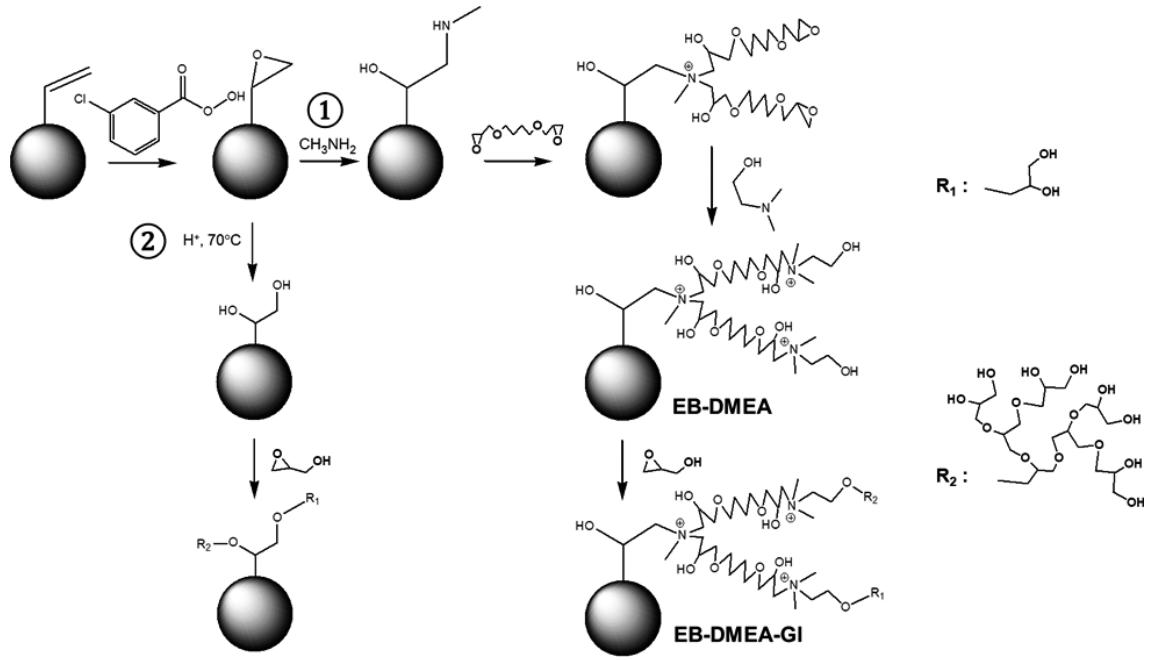

Fig. 1. Scheme of the preparation and expected structures of resins EB-DMEA and EB-DMEA-Gl (R_1, R_2 are possible substituents that can be formed during glycidol polymerization in the functional layer)

oxy groups as compared to methylamine amount. At the same time, glycidol addition and activation of its polymerization led to a decrease in ion-exchange capacity. This effect is caused by the polymerization of glycidol around the ion-exchange sites and, consequently, by steric hindrances.

For evaluating the effect of anchor groups nature, the parameters reflecting the degree of hydrophilization and substrate shielding [15, 21, 27] were estimated for the obtained phases (Table 1). Resin EB-DMEA x5 with higher capacity and a predominant number of anchor amino groups possessed lower values of these parameters as compared to EB-DMEA x1. A significant decrease in $\alpha(BrO_3^-/Cl^-)$ and $\alpha(ClO_3^-/Cl^-)$ reflects better substrate shielding and indicates the need to increase the number of sites for the attachment of the functional layer. Resin EB-DMEA x5 had higher efficiency up to 41,000 tonf/m among all obtained in this work phases. However, much lower efficiency values for polarizable anions in comparison with chloride (Table 2) indicate substantial remaining influence of nonionic interactions. Conducting the additional step of glycidol treatment allowed the increase of hydrophilization and shielding degree (see Table 1), still the impact of nonion-exchange interactions was significant.

Generally, obtained resins can be characterized as phases with medium hydrophilicity and shielding degree. They have similar hydrophilicity to phases based on acylated PS-DVB with grafted modified polyethylenimine [15], however simpler functional layer of synthesized resins doesn't provide such effective substrate shielding. Phases based on the same epoxidized substrate with grafted polyethylenimine modified with polyglycidol [14] or with polyelectrolytes [25] are superior not only in shielding, but also in hydrophilization degree. As a result, obtained in this work phases did not allow one use them for the determination of highly polarizable anions in contrast to resins with

Table 1. Capacities and selectivity coefficients reflecting the degree of hydrophilization and substrate shielding in IC mode (eluent: 1 mM KOH for EB-DMEA x1 and EB-DMEA x1 Gl, 8 mM KOH for EB-DMEA x5, and 5 mM KOH for EB-DMEA x5 Gl)

Phase	EB-DMEA x1	EB-DMEA x1 Gl	EB-DMEA x5	EB-DMEA x5 Gl
Capacity, μmol/g	26	14	61	48
$\alpha(NO_3^-/Cl^-)$	4.86	4.06	3.53	3.13
$\alpha(NO_3^-/Br^-)$	1.52	1.38	1.49	1.37
$\alpha(BrO_3^-/Cl^-)$	2.41	1.77	1.72	1.52
$\alpha(ClO_3^-/Cl^-)$	8.17	6.09	5.67	4.61
$\alpha(ClO_3^-/NO_3^-)$	1.68	1.50	1.60	1.47

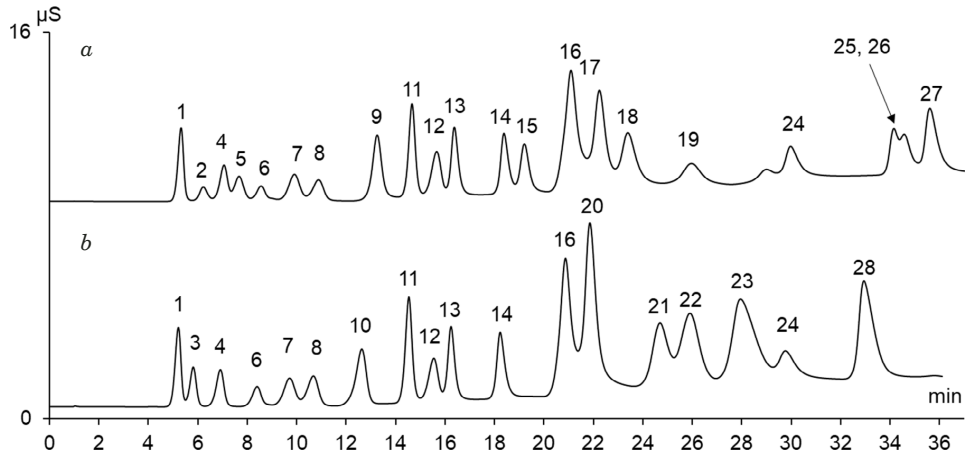

Fig. 2. Chromatogram of anions mixtures on the stationary phase EB-DMEA x5: *a* — eluent 1 mM KOH — 0 – 11 min, 1 – 7 mM KOH — 11 – 18 min, 7 – 20 mM KOH — 26 – 34 min; *b* — 1 mM KOH — 0 – 11 min, 1 – 7 mM KOH — 11 – 18 min, 7 – 12 mM KOH — 26 – 34 min (flow rate: 1 ml/min; *1* — fluoride; *2* — gluconate; *3* — iodate; *4* — glycolate; *5* — galacturonate; *6* — formate; *7* — lactate; *8* — chloride; *9* — methylsulfonate; *10* — chlorite; *11* — nitrite; *12* — propionate; *13* — bromide; *14* — nitrate; *15* — monochloroacetate; *16* — sulfate; *17* — oxalate; *18* — maleate; *19* — adipate; *20* — selenate; *21* — tungstate; *22* — molybdate; *23* — chromate; *24* — phosphate; *25* — citrate; *26* — isocitrate; *27* — trans-aconitate; *28* — arsenate)

grafted polyethyleneimine [14, 15, 29] or polyelectrolytes [22].

Glycidol polymerization expectedly led to a decrease in selectivity, especially for organic acids. Due to the highest capacity, efficiency and selectivity resin EB-DMEA x5 was used for the separation of multicomponent mixtures by suppressed IC. In gradient elution mode it allowed the separation of 7 common anions simultaneously with 13 organic acids in 37 min (Fig. 2, *a*) or with 11 anions including oxyanions, namely selenate, molybdate, chromate, tungstate and arsenate, in 35 min (Fig. 2, *b*). Proposed approach made it possible to obtain adsorbent with higher separation ability and efficiency as a result of less time-consuming synthesis as compared to phases based on the same epoxidized PS-DVB with grafted modified polyethyleneimine [14, 25].

Table 2. Efficiency and asymmetry factors for analytes in different modes of HPLC on a column EB-DMEA x5 (eluent: 8 mM KOH for IC, CH_3CN — 20 mM ammonium formate buffer solution pH 3.0 (90:10, v/v) for HILIC, CH_3CN — water (70:30, v/v) for RP HPLC; flow rate: 1 ml/min)

Analyte	*N*, tp/m	*As*
	IC	
Cl^-	41000	1.1
Br^-	26000	1.5
NO_3^-	19500	1.8
	HILIC	
Uracil	23000	0.9
Cytidine	19000	0.9
Guanosine	15000	1.0
	RP HPLC	
Benzene	17000	1.2
Propylbenzene	14000	1.1
Hexylbenzene	12000	1.3

In HILIC mode Tanaka test for the obtained adsorbents was performed in same way as in works [12, 14, 15, 25] with water as a marker of void volume. All phases had low hydrophilicity $k(U)$ and selectivity toward hydroxyl groups α(OH) (Table 3), which is consistent with their low hydrophilicity in IC mode. Hydrophilicity of synthesized resins was much lower as compared to PS-DVB-based hyperbranched mixed-mode phase ($k(U) = 7.2$) [12], polyethyleneimine-grafted phases ($k(U)$ from 1.1 to 1.57) [15] and a resin based on the same epoxidized PS-DVB with grafted polyethyleneimine and polyelectrolytes ($k(U) = 3.18$) [25]. The parameters $k(U)$ and α(OH) grew with the increase in the number of anchor amino groups for both types of phases EB-DMEA and EB-DMEA Gl. Polymerization of glycidol did not affect the parameters of Tanaka test except for α(AX) and α(CX). Their decrease on phases EB-DMEA x1 Gl and EB-DMEA x5 Gl confirms higher degree of shielding with polyglycidol and corresponds to $\alpha(BrO_3^-/Cl^-)$ decrease in IC mode. Generally, the change in α(AX) correlates with capacity change in IC mode, although hydrophobic interactions still influence *p*-toluenesulfonate retention. For all phases except EB-DMEA x5 Gl α(CX) > 0, namely the positively charged trimethylphenylammonium chloride was not repulsed in contrast to previously obtained phases based on the same PS-DVB substrate [15, 25]. Presumably, epoxy groups on the surface of PS-DVB can be partly oxidized to carboxyl groups, which provide the retention of positively charged trimethylphenylammonium chloride. Shielding the substrate surface by polyglycidol

(resin EB-DMEA x5 Gl) or polyethyleneimine [25] helps to eliminate the influence of negatively charged carboxyl groups.

The most hydrophilic resin according to Tanaka test was chosen to demonstrate the possibility of using obtained stationary phases in HILIC mode. Despite lower $k(U)$ and retention factors of nitrogenous bases and nucleosides the column EB-DMEA x5 had higher efficiency (see Table 2) as compared to phases with grafted modified polyethylenimine [15, 25]. Consequently, resin EB-DMEA x5 provided fast separation of 6 nucleosides and nitrogenous bases in less than 5 min with efficiency up to 23000 tp/m (Fig. 3, *a*).

Phase EB-DMEA x5 demonstrated significantly lower retention of alkylbenzenes in RP HPLC mode as compared to the most hydrophilic resin on the base of acylated PS-DVB with covalently attached hyperbranched layer described in work [12]. It is another evidence of the increased hydrophilization degree of the epoxidized substrate. Even a relatively simple functional layer on the surface of epoxidized PS-DVB can substantially reduce the retention of hydrophobic analytes as compared to adsorbents based on acylated substrate with complex layers. Resin EB-DMEA x5 made it possible to separate a mixture of 7 alkylbenzenes in 13 min using 30:70 v/v water: acetonitrile as a mobile phase with efficiency up to 17000 tp/m (see Fig. 3, *b*, Table 2). Hyperbranched phase provided the separation of the same analytes only in 35 min [12].

Thus, PS-DVB epoxidation and further grafting of branched layers on its surfaces is a promising tool to obtain mixed-mode resins for three HPLC modes. High separation ability and efficiency of phase with increased amount of anchor amino groups allowed its use for separation of multicomponent mixtures in suppressed IC mode. The same stationary phase also provided the separation of nitrogenous bases and nucleosides in HILIC mode and alkylbenzenes in RP HPLC. The obtained phase showed higher separation ability in IC mode and higher efficiency in HILIC mode as compared to previously described resins based on

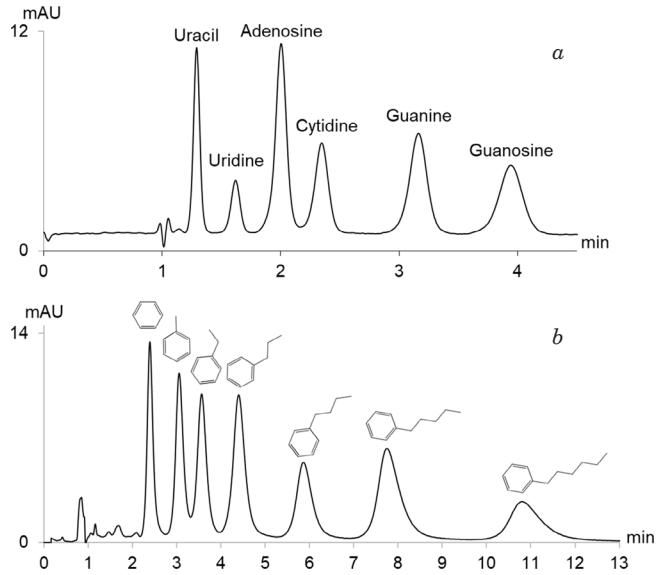

Fig. 3. Chromatogram of nucleosides and nitrogenous bases mixture in HILIC mode (*a*) and alkylbenzenes mixture in RP HPLC mode (*b*) on the stationary phase EB-DMEA x5 (conditions are the same as in Table 2)

acylated or epoxidized PS-DVB with grafted polyethyleneimine modified with glycidol or polyelectrolytes [14, 15, 25]. On the other hand, synthesis procedure of novel resin was simpler and much faster than polyethyleneimine-grafted phases.

Conclusion

The approach to PS-DVB epoxidation and further grafting of branched layers allowed obtaining an efficient and selective mixed-mode stationary phase. The advantage of increasing the number of anchor amino groups for the hydrophilization growth of the resins was demonstrated in HILIC and IC modes. An additional increase in the shielding degree of the phases was achieved by the polymerization of glycidol in branched functional layer. The resin with the highest ion-exchange capacity provided the separation of up to 20 anions in gradient elution mode of IC, 6 nucleosides and nitrogenous bases by HILIC, and 7 alkylbenzenes by RP HPLC. Obtained phase was superior in terms of synthesis duration, separation ability of anions in

Table 3. Tanaka tests parameters (eluent: CH_3CN — 20 mM ammonium acetate buffer solution pH 4.7 (90:10, v/v), flow rate 0.5 ml/min)

Phase	EB-DMEA x1	EB-DMEA x1 Gl	EB-DMEA x5	EB-DMEA x5 Gl
$k(U)$	0.54	0.52	0.73	0.72
α(OH)	1.49	1.48	1.74	1.77
$\alpha(CH_2)$	1.02	1.03	1.09	1.09
α(V/A)	1.16	1.17	1.24	1.26
α(CX)	1.03	0.36	0.68	0
α(AX)	39.0	25.8	119.8	87.6
α(Tb/Tp)	0.60	0.64	0.34	0.38

supressed IC mode and efficiency in HILIC mode as compared to previously reported PS-DVB-based mixed-mode stationary phases with grafted modified polyethyleneimine [14, 15, 25].

Acknowledgments

This work was supported by Russian Scientific Foundation through the grant N 20-13-00140 using the equipment of the Central Collective Use Center of Moscow State University "Technologies for Obtaining New Nanostructured Materials and Their Comprehensive Study," acquired by Moscow State University under the program for updating the instrumentation base within the framework of the national project "Science" and within the framework of the Development Program of Moscow State University.

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